ON THE ELECTRONIC SPECTRA OF BENZYL ACETATE IN DIFFERENT STATES

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(Plate 7)

ABSTRACT. The results on the investigation of the ultraviolet absorption spectra of benzyl acetate in the gaseous, liquid and solid states and in solutions in ethyl alcohol and cyclohexane are reported and an analysis of the observed band system is presented. It is shown that, the benzyl acetate molecule belongs to the point group C_s and the absorption is due to the $A'-A'$ transition of the π-electron system. It has also been observed that in the liquid state and in solutions in ethyl alcohol and cyclohexane the 0, 0 band due to the free molecule is shifted towards the longer wavelength by about 700 cm^{-1}. With solidification of the liquid and cooling to $-180°C$, a further shift of the 0, 0 band by 81 cm^{-1} in the same direction occurs.

INTRODUCTION

From an analysis of the luminescence band system excited by the Hg 3650 Å group of lines in pure benzyl acetate and in solutions in CCl_4, $HCCl_3$, and EtOH in the solid state at $-180°C$, it was concluded (Bag, 1966) that the bands originate from the emission from a metastable state of the molecule. It was suggested that the meta-stable state is formed due to the singlet–triplet π-electron absorption of the molecule. A perusal through the existing literatures showed that there were no data on the absorption spectra of benzyl acetate except those on the absorption spectrum of solution of benzyl acetate in cyclohexane (Berlman, 1965). It was, therefore, decided to investigate the ultraviolet absorption spectra of benzyl acetate in the vapour, liquid and solid states and in solutions in different solvents. The results of this investigation together with a discussion of the results are presented in this paper.

EXPERIMENTAL

Two samples of chemically pure benzyl acetate were obtained from Rhodia (France) and Fluka (Switzerland). Each of the samples was carefully fractionated and proper fractions were distilled under reduced pressure. In order to test the purity of the samples the absorption spectrum of the samples in cyclohexane of specpure quality were studied with a spectrophotometer and the results obtained were found to be identical with those reported by Berlman (1965).

The experimental arrangements for studying photographically the absorption spectra of benzyl acetate in the vapour phase at different temperatures, in the

liquid state at room temperature, in the solid state at −180°C and in solutions in specpure cyclohexane and ethyl alcohol were the same as used by earlier workers (Banerjee, 1956; Sirkar and Misra, 1959). In the case of vapour, absorption tubes of lengths 30 cms, 50 cms and 100 cms provided with plane quartz windows were used while in the case of solutions the absorption spectra were obtained with sintered quartz cells of thickness 1.0 cm and 0.5 cm. Adam Hilger all metal E1 spectrograph (E478) having dispersion of about 2.5 Å/mm in the region 2600 Å was used to obtain the absorption spectra which were photographed on Kodak spectrum analysis no. 1 film. Along with each absorption spectrum Iron arc spectrum was also photographed with a Hartmann diaphragm on the same film for comparison. Microphotometric records of the spectra were obtained on a Kipp and Zonen Moll microphotometer. The method of determination of the positions of the absorption maxima was the same as given by Banerjee (1956). The accuracies in the measurements of the positions of the absorption peaks were ± 5 cm^{-1} for sharp bands and ± 10 cm^{-1} for moderately sharp bands, while the uncertainty in the case of the broad and diffuse bands was larger than ± 10 cm^{-1}.

RESULTS

The microphotometric records of the absorption spectra of benzyl acetate in the vapour, liquid and solid states and in solutions in cyclohexane and ethyl alcohol are reproduced in figures 1 and 2 (Plate 7). The positions of the absorption maxima, their relative intensities and probable assignments are given in tables 1, 2 and 3.

Table 1

Ultraviolet absorption spectra of benzyl acetate in the vapour phase

Wave number (cm^{-1}) and intensity		Assignment	Wave number (cm^{-1}) and intensity		Assignment
95°C	75°C		95°C	75°C	
37347 (ms)	37347 (w)	0−737		39242 (ms)	0+1158
37526 (s)	37526 (m)	0−558	Complete		0+226+937
37910 (vs)	37910 (s.sh)	0−174	absorption to	39522 (w)	0+1438
38084 (vs)	38084 (s)	0, 0	shorter wave		0+552+937
Complete	38310 (m)	0+226	lengths	39608 (w)	0+1524
absorption at	38516 (m)	0+432			0+2×777
the shorter	38636 (vw)	0+552		39789 (sb)	0+1705
wave lengths	38861 (vs)	0+777			0+777+937
	39021 (vs)	0+937		39964 (sb)	0+2×937
				40221 (wb)	0+226+2×937
					0+937+1158
				40449 (w)	0+3×777

The strengths of the absorption are marked as s-strong; w-weak; v-very; m-medium; b-broad and sh - shoulder.

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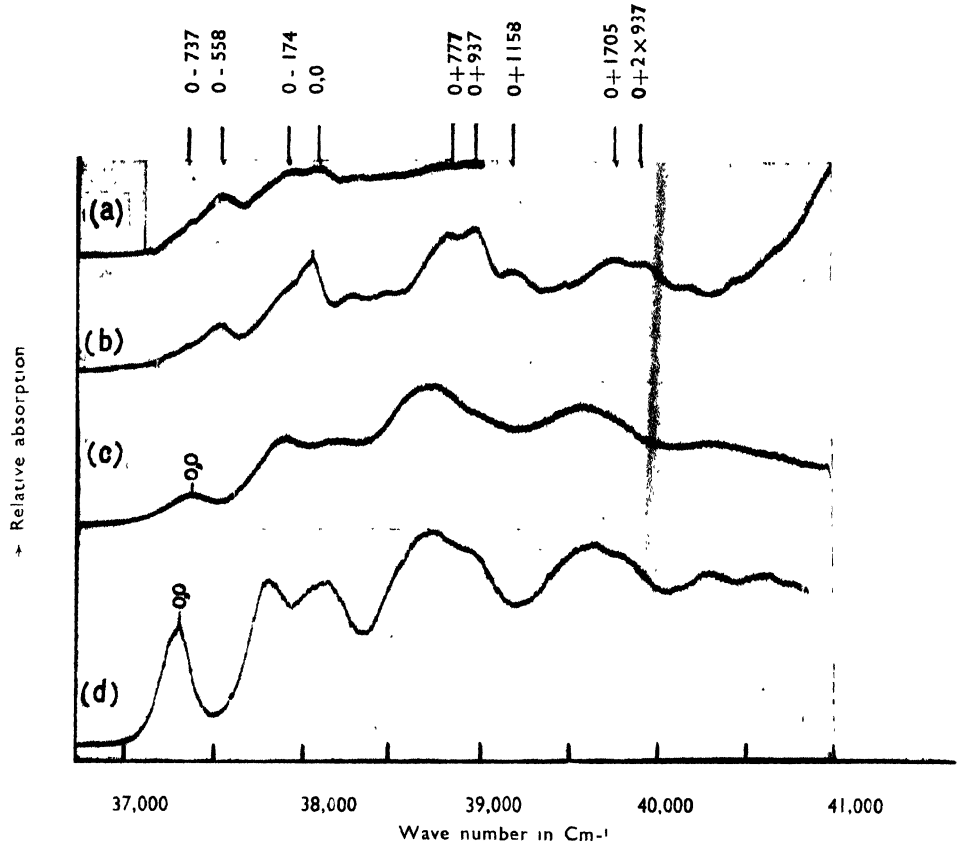

Figure 1. Microphotometric records of the ultraviolet absorption spectra of benzyl acetate
(a) Vapour at 95°C showing cut off from about 38200 cm-1
(b) Vapour at 75°C (c) Liquid at 32°C (d) Solid at—180°C

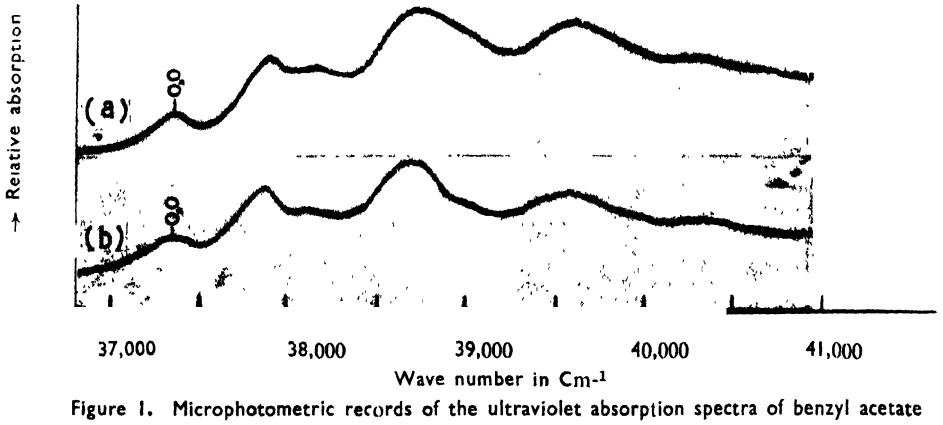

Figure 2. Microphotometric records of the ultravio et absorption spectra of benzyl acetate in solutions :
(a) 5.0×10^{-3}M solution in ethyl alcohol; (b) 1.03×10^{-3}M solution in cyclohexane

Table 2

Ultraviolet absorption spectra of benzyl acetate in the liquid and solid states

Liquid 32°C		Solid −180°C	
Wave number (cm^{-1}) and intensity	Assignment	Wave number (cm^{-1}) and intensity	Assignment
37397 (m)	0, 0	37316 (s)	0, 0
37948 (s)	0+551	37889 (vs)	0+573
38276 (ms)	0+879	38229 (vs)	0+913
38823 (vs)	0+1426 0+551+879	38823 (vs) 39035 (s.sh)	0+1507 0+1719
39081 (w)	0+1684		
39694 (s)	0+1426+879	39749 (s) 39932 (s.sh)	0+913+1507 0+913+1719
40506 (m)	0+1426+1684	40384 (ms) 40721 (m)	0+2×1507 0+2×1719

Table 3

Ultraviolet absorption spectra of benzyl acetate in solutions at 32°C

(a) Solution in Cyclohexane (1.03×10^{-3}M)		(b) Solution in Ethyl Alcohol (5.0×10^{-3}M)	
Wave number (cm^{-1}) and intensity	Assignment	Wave number (cm^{-1}) and intensity	Assignment
37330 (m)	0, 0	37341 (m)	0, 0
37882 (s)	0+552	37910 (s)	0+579
38171 (ms)	0+841	38193 (ms)	0+852
38763 (vs)	0+1433	38789 (vs)	0+1449
39058 (ms)	0+2×841 0+1728	39043 (m.sh)	0+1702 0+2×852
39607 (s)	0+841+1433	39667 (s)	0+852+1449
40327 (m)	0+2×1433	40383 (ms)	0+2×1449 0+1449+1702
		40712 (w)	0+2×1702

DISCUSSION

(a) *Absorption spectrum in the vapour phase*

The absorption spectrum of benzyl acetate at room temperature (about 32°C) in an absorption tube of length 100 cms shows a number of weakly developed bands in the region of 2670 Å—2500 Å corresponding to the $\pi-\pi^*$ transition in monosubstituted benzenes. The bands show fairly sharp heads towards shorter wavelength side and are all degraded to the higher wavelengths. The strongest band on the long wavelength side is at 38084 cm^{-1} which appears with undiminished intensity at lower pressure of the vapour. At 75°C the number as well as the intensities of the bands increase but they become more diffuse (figure 1b). With the increase of temperature of the vapour to 95°C, the bands at 37347, 37526 and 37910 on the long wavelength side of the 38084 cm^{-1} band gain in intensity and become more prominent but from about 38200 cm^{-1} towards the shorter wavelengths complete absorption sets in (figure 1a). At a still higher temperature of 120°C complete absorption begins at a still lower frequency.

From these observations of temperature dependence of intensities of the bands the strong band at 38084 cm^{-1} in the spectrum of the vapour at 75°C is taken to be 0, 0 band while the bands at 37910, 37526 and 37347 cm^{-1} are assigned to $v\rightarrow 0$ transitions involving the ground state frequencies 174, 558 and 737 cm^{-1} respectively, of the molecule. The higher intensities of these three bands at 95°C are due to the increase in their Boltzman factors as a result of increase in the number of absorbing molecules. On the other hand, the bands on the shorter wavelength side have been assigned to transitions involving fundamental excited state frequencies 226(254), 432(482), 552(620), 777(825), 937(1002), 1158(1214), 1439(1485), 1525(1605) and 1705(1730) cm^{-1} and their combinations and overtones. The figures in parentheses give the corresponding ground state frequencies of the benzyl acetate molecule reported by Chattopadhyay and Mukherjee (1966). It is seen from table 1 that some of the bands could be given more than one assignment which seems justified on the consideration of the intensities of these bands.

Chattopadhyay and Mukherjee (1966) assigned the vibrational frequencies of benzyl acetate molecule under the assumption of an approximately C_{2v} symmetry of the molecule. In that case, the $\pi-\pi^*$ electronic transition is A_1-B_2 and assuming no vibronic interaction only $v\rightarrow 0$ and $0\rightarrow v'$ transitions involving totally symmetric vibrational frequencies would be expected to appear in absorption at moderate temperature. However, the appearance of the moderately intense bands involving the ground state frequencies 178, 558 and 737 cm^{-1} and the excited state frequency 226 cm^{-1} which all belong to the non-totally symmetric species of the molecule, are contradictory to this theoretical expectation. On the other-hand, if the molecule is assumed to belong to the point group C_s with the acetate group in the plane of the phenyl ring, the electronic transition is $A'-A'$. Under

this condition all transitions involving totally and non-totally symmetric vibrations (under the assumption of approximate C_{2v} symmetry) will appear in absorption with varying intensities depending on the actual value of the transition moments. This conclusion is in agreement with the assignments given in table 1.

Thus it is concluded that the benzyl acetate molecules belong to the point group with symmetry C_s and the observed absorption is due to an $A'-A'$ π-electron transition.

(b) *Absorption spectra of the liquid solid and solutions* :

With the liquefaction of the vapour, the band system becomes more diffuse and the number of bands diminishes (figure 1c). The band at 37397 cm^{-1} is taken as the 0, 0 band and the other bands are assigned to transitions involving the frequency differences 551, 879, 1426 and 1682 cm^{-1} and their combinations (table 2). The 0, 0 band of the liquid is thus shifted towards the higher wavelength side by 687 cm^{-1}. In the case of 5×10^{-3}M solution of benzyl acetate in ethyl alcohol and 1.03×10^{-3}M solution in cyclohexane, the 0, 0 band shifts to long wavelength side by 754 cm^{-1} and 743 cm^{-1} respectively, with respect to the 0, 0 band in the vapour state (figure 2). As can be seen from tables 2 and 3, the excited state frequencies observed in the spectra of solutions compare favourably with those observed in the spectrum of the pure liquid. The results indicate the influence of environment on the electronic energy levels of the free molecule.

It is seen from figure 1d that the absorption spectrum of the solid at $-180°C$ differs only slightly from that of the liquid. In general, the bands become sharper and more intense and two more bands at 39932 and 40721 cm^{-1} appear in the spectrum. The assignments of the bands with the band at 37316 cm^{-1} taken as the 0, 0 band are given in table 2. It is seen from the table that the values of the frequency differences involved in these transitions are somewhat larger than those in the liquid and are more in agreement with the frequencies due to the vapour state. Moreover, the 0, 0 band in the solid state is shifted further towards longer wavelength side by 81 cm^{-1} with respect to the 0,0 band in the liquid state.

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